

Preparation and Characterization of Aromatic Amine Cured Epoxy-Silica Hybrid Inorganic-Organic Coating via In Situ Sol-gel Process

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ABSTRACT

The organic-inorganic hybrid coating based on epoxy resin and tetraethoxysilane have been prepared and studied. These hybrid network possess excellent optical transparency and nano scale microphase separation. These hybrid materials can be used for coating aluminum alloy (AA) substrates. Formation of the inorganic phase, from tetraethoxysilane (TEOS) by sol-gel process, organic phase and hybrid network were characterized by Fourier Transform infrared (FTIR), attenuated total reflectance infrared (ATR-IR), and ²⁹Si NMR spectroscopic techniques, and thermal gravimetry analysis (TGA) methods. The Chemical structure of obtained network affects morphology of the coating. So, morphology of the fractured surface was observed by scanning electron microscopy (SEM). It is found that the average diameter of particles is 167 nm, which indicates the transparency of the hybrid system. TGA results show that cross-linking between the epoxy resin and silica increases the thermal stability of the system.

Key Words:

Sol-gel process;
hybrid inorganic-organic;
tetraethoxysilane;
epoxy resin.

INTRODUCTION

In recent years, new kinds of inorganic-organic hybrid materials have been prepared via sol-gel process. These hybrids are also like nanocomposites because of the small size of formed inorganic structure, usually of the nanometer size and are

often optically transparent systems. The sol-gel process is of interest in preparing these materials due to its mild conditions such as low temperature and pressure. This process provides a convenient route to combine inorganic and organic components as

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a homogeneous hybrid material. Many researches have demonstrated that, monolithic transparent hybrid materials without macroscopic phase separations can be prepared by controlling properly the conditions of hydrolysis and condensation of sol-gel materials such as tetraethoxysilane (TEOS)[1-3]. In these hybrid materials, organic and inorganic components can be chemically bonded or just physically mixed. A significant feature to enhance compatibility in hybrid materials is the formation of covalent bonding between organic-inorganic polymers and inorganic components [4-9].

The specific mechanical properties of sol-gel materials are affected by particle size and interfacial interaction between dispersed and continuous phases. Furthermore compatibility of organic and inorganic hybrid materials are influenced by solvents, coupling agents, and network structures[9-11].

Hybrid inorganic-organic (nanocomposite) offer a variety of advantageous properties in various applications. They can be employed as optical materials with high reflective indices, colored glasses, hard coatings, corrosion protection coatings on the aluminum surfaces, porous materials for chromatography and catalyst supports, and aerogel. Combination of hardness of an inorganic phase and toughness of an organic phase make such systems interesting also from the aspect of mechanical behaviour. [12-14,4,6].

We have prepared and studied an interpenetrating network (IPN) of the organic-inorganic hybrid system composed of an organic component and an inorganic silica structure formed by a sol-gel process from TEOS. The existence of inorganic phase increases mechanical properties such as scratch resistance; and the existence of organic phase increases the adhesion of hybrid coating, which is transparent to substrate. This property can be mostly conserved until material's heterogeneity remains below 400nm [12]. Organic system was represented by a stoichiometric epoxide-aromatic amine network, prepared from GY250 (diglycidyl ether of bisphenol A) and Araldite HY 850 (aromatic amine). The in-situ built-in inorganic phase results the reinforcement of this network.

During polymerization grafting between the epoxide network and silica-siloxane structures also take place by condensation of silanol groups with the C-OH group formed at epoxide-aromatic amine reaction.

The goal of this paper is to investigate the forma-

tion of GY250-HY850-TEOS hybrid and to determine its structure by FTIR, ATR-IR, and ^{29}Si NMR spectroscopic methods. Moreover, the effect of chemical structure and morphology of the product (IPN) has been investigated with scanning electron microscopy (SEM). The thermal stability has been studied also by thermal gravimetry analysis (TGA) method. This hybrid, was coated on the 1050 aluminum alloy (AA) substrate by dip coating method and its ATR-IR spectrum was studied.

EXPERIMENTAL

Materials

Organic system components

Organic phase was prepared by curing GY250 (diglycidyl ether of bisphenol A, DGEBA) with Araldite HY 850 (aromatic amine) Ciba-Geigy (Scheme I). Equivalent of functional groups for the epoxy group in the GY250 was $E_E = 183 \text{ g/mol}$, viscosity = 9000-12000 mPa, and the index of amine = 4,40, and its viscosity = 15000-21000 mPa.

Inorganic system components

Tetraethoxysilane (TEOS) Fluka, (99.3%, GC analysis) (Scheme I), hydrochloric acid 37% (HCl) Merck and Ethanol (ETOH) Merck.

Substrate for coating

Aluminum alloy (AA) of 1000 series has minimum percent component alloys. It can be considered as pure aluminum. In this work, we have used 1050 series aluminum alloy as substrate (from Arak Aluminum Rolling Co).

Synthesis of epoxy-silica hybrid network

It was prepared by sol-gel process. Hydrolysis and condensation of TEOS were performed in ethanol (ETOH) solutions at a molar ratio of $\text{TEOS}/\text{H}_2\text{O} = 1/1$ in $\text{pH}=2$. The epoxy network reaction was catalyzed by the polymer base catalyst HY850 used as a curing agent of the epoxy. IPNs were prepared with two stages simultaneous process as follows:

1. TEOS was hydrolyzed by acid catalyst in the mixture of $\text{TEOS}-\text{H}_2\text{O}-\text{ETOH}-\text{HCl}$ at room temperature for 1 h.

2. In the second stage the prehydrolysed TEOS was mixed with the organic component GY250-HY 850 to start the "simultaneous" formation of both organic and inorganic polymer phases. In fact the sol-gel process is faster and silica structures formed prior to the epoxy system. The first stage of the sol-gel process was catalyzed by the acid at PH=2 and the second stage by the polymer which was in excess.

Aluminum surface preparation and dip coating method
 1050 aluminum alloy (AA) substrates were prepared for dip coating in the following stages:

First it is polished, by using 400-600 grit and sand papers and then it is immersed in a 0.01M NaOH solution and secondly, in a 0.01 M HCl solution and finally immersed in a methanol and hexane solution.

Cleaned AA substrates were dipped into the sol system, manual for 1 minute, following by vertical withdrawing at constant speed (Figure1).

After this treatment, A thin film layer of hybrid coating was formed on the 1050 aluminum alloy (AA) substrate. Finally, the curing schedule was performed as follows:

The coated 1050 aluminum alloy samples predried at room temperature for 24 h, and cured at 120°C for completing curing condition. Monolayer coating was carried out using a dip coating techniques on the glass slide as substrate. This hybrid coating is transparent like uncoated glass slide.

Instruments and Characterization

The chemical structure of the prepared samples were

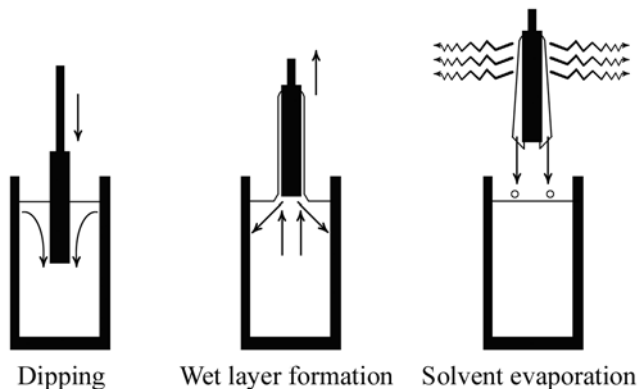


Figure 1. Stages of dip coating process.

identified by FTIR and ATR-IR which were recorded on a Bruker IFS48 FTIR spectrometer and ²⁹Si NMR Spectra, were recorded by a Bruker DSX-500 WB. For FTIR analysis, KBr pressed into pellets, and then each sample set over each of them. ATR-IR spectra of hybrid epoxy-silica over the aluminum surface were recorded, using KRS5 cell with angle 15°. The DMSO-d₆ used as solvent for ²⁹Si NMR spectroscopy.

Thermal properties were characterized by Perkin Elmer Pyris1. TGA was performed at a heating rate of 10°C/min for each sample. The measurements on inorganic phase were carried out under nitrogen atmosphere, whereas for hybrid material were performed under air.

Morphology of the fractured surfaces of hybrid materials were observed by SEM Cambridge S-360. It should be mentioned that all characterization tests were carried out at Iran polymer and Petrochemical Institute.

RESULTS AND DISCUSSION

The sol-gel reactions (Figure 2) are catalyzed by acid (HCl). Grafting of the epoxide on silica network is also an important factor in controlling the hybrid morphology as it promotes miscibility and affects phase separation. IR results indicate that covalent bonds are formed between inorganic and organic networks. It should be mentioned that the aromatic amine agent reacts with the major portion of GY 250 (DGEBA) and open the ring of epoxy group (Figure 3). Then, the reaction of SiOH groups of hydrolyzed silica-siloxane cluster and C-OH group of the organic network result in hybrid network.

FTIR results

In Figure 4 the FTIR spectra of inorganic and organic hybrid before and after curing and also inorganic and organic phases are shown.

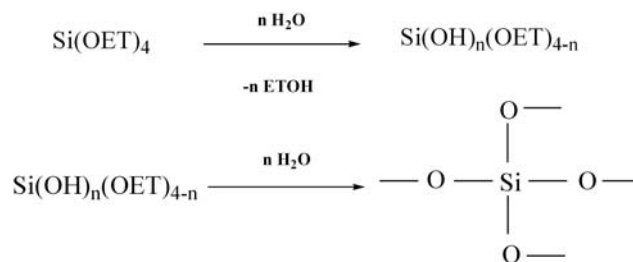


Figure 2. The sol-gel reaction of TEOS.



Figure 3. cross-linking reaction of Si-O of tetraethoxysilane and C-O of epoxy group.

The characteristic peaks of hybrid before curing (Figure 4a) indicate the formation of Si-O-Si bonds: ν_{as} Si-O at 1082 cm^{-1} , ν Si-OH at 996 cm^{-1} , ν_{s} Si-O at 793 cm^{-1} and 471 cm^{-1} were seen in the FTIR spectra. The presence of the ethoxy group was proved in all spectra by absorption bands of ν_{as} CH_3 and ν_{as} CH_2 at 2974 cm^{-1} , 2928 cm^{-1} , respectively and other specific peaks in the range of $1248\text{--}1485\text{ cm}^{-1}$. C=C vibrations for benzene ring at 1510 cm^{-1} and 1607 cm^{-1} were also observed. Bending vibration of methylen group at 1391 cm^{-1} and bending vibration of methyl group at 1364 cm^{-1} were appeared. The absorption band of epoxy group at 916 cm^{-1} was decreased but was not disappeared. Absorption at 831 cm^{-1} was related to aromatic substitutions. Stretching vibrations of N-H and C=C aromatic bond appeared at 3371 cm^{-1} and 1726 cm^{-1} , respectively.

FTIR spectra of hybrid after curing in mould (Figure 4b) indicated the disappearance of the peak of epoxy group, and so the epoxy ring opening. Instead, the absorption band of Si-O-C at 1096 cm^{-1} was observed. The amine band at 1514 cm^{-1} and C=C aromatic bands at 1610 cm^{-1} and 1724 cm^{-1} were

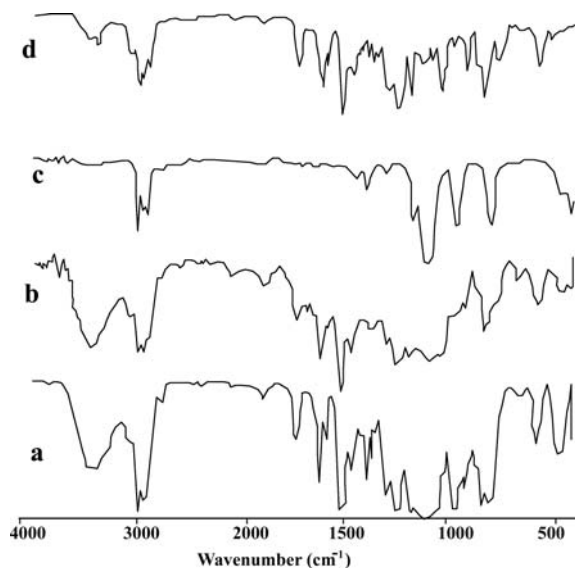


Figure 4. FTIR spectra of The hybrid: a) before and b) after curing and c) the inorganic and d) organic phases.

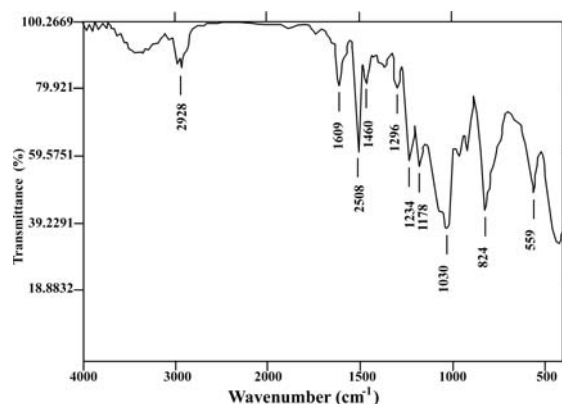


Figure 5. ATR-IR spectra of hybrid inorganic-organic coating on the aluminum alloy (AA).

appeared, respectively. In addition, stretching vibrations of C-H at 2928 cm^{-1} and 2966 cm^{-1} were observed.

The FTIR spectrum of inorganic phase (TEOS- H_2O -HCl-ETOH) (Figure 4c), is characterized by the following absorption bands: ν_{as} Si-O at 1115 cm^{-1} , ν Si-O-C at 1082 cm^{-1} , ν Si-OH at 968 cm^{-1} , and ν_{s} Si-O at 793 cm^{-1} , and 470 cm^{-1} , respectively. Beside these characteristic bands of the inorganic network, the ethoxy groups were appeared in all spectra by the following absorption bands: ν_{as} CH_3 , ν_{as} CH_2 at 2978 cm^{-1} and 2930 cm^{-1} , respectively, and other specific bands in the range of $1298\text{--}1485\text{ cm}^{-1}$ were also appeared.

The FTIR absorptions bands of the organic phase (Figure 4d) are as follows: stretching vibrations of C-H at 2928 cm^{-1} and 2966 cm^{-1} , C=C vibrations for benzene ring at 1510 cm^{-1} and 1607 cm^{-1} , respectively. The absorption peak of epoxy group at 914 cm^{-1} was also appeared [15-17].

ATR-IR spectrum of nanocomposite hybrid coating on aluminum alloy (AA)

The ATR-IR spectrum of the hybrid inorganic-organic

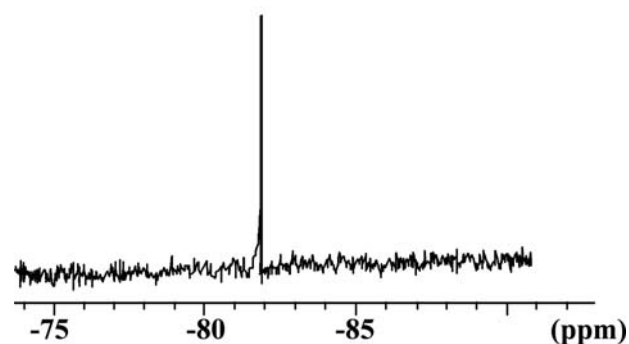
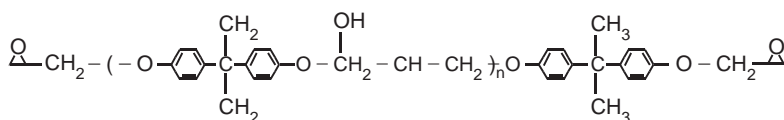


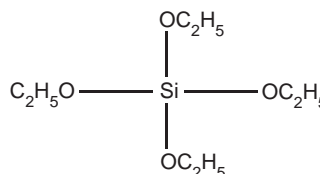
Figure 6. ^{29}Si NMR spectrum of tetraethoxysilane (TEOS).

Chemical structure of materials used

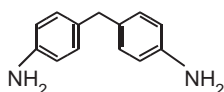
Epoxy:DGEBA:Araldite Gy250



Silica: Tetraethoxysilane (TEOS)



Curing agent: HY850: Aromatic amino adduct



Adduct aromatic amino based on 4,4diaminodiphenylmethane

Scheme 1

coating on aluminum alloy (AA) is shown in (Figure 5). The absorption band of epoxy ring is disappeared and instead C-O-Si absorption is observed at 1030 cm^{-1} . In this spectrum, absorption at 824 cm^{-1} relates to aromatic substitutions, and absorption bands at 1234 cm^{-1} relate to Si-O-H. Also C=C vibration bands of benzene ring at 1508 cm^{-1} and 1607 cm^{-1} were observed [17,18].

²⁹Si NMR spectrum of inorganic phase and hybrid organic-inorganic before curing,

In Figure 6, the ²⁹Si NMR spectrum of tetraethoxysilane is shown for pure TEOS, and $\delta = -81/7\text{ ppm}$ was assigned. In Figure 7 the ²⁹Si NMR spectrum of hydrolysed products of tetraethoxysilane is shown. As it is obvious from these figures, ²⁹Si NMR chemical shifts in the case of TEOS ($\delta = -83.91$) appeared at the most negative value i.e., -74.26 ppm relates to

Si(OH)₄, -76.42 ppm to Si(OET)(OH)₃, -78.91 ppm to Si(OET)₂(OH)₂, -81.91 ppm to Si(OET)₃(OH), and -86.71 ppm to Si-O-Si(OET)(OH)₂.

In Figure 8 the ²⁹Si NMR spectrum of the hybrid organic-inorganic is shown. Taking into account the inductive effect, it could be predicated that the ²⁹Si NMR chemical shifts of the organic substituted at -73.928 ppm relates to Si(OH)₄, -76.108 ppm to Si(OET)(OH)₂, -78.621 ppm to Si(OET)₂(OH)₂, and -85.812 ppm to Si-O-Si(OET)(OH)₂.

The fact is, that the value of ²⁹Si NMR chemical shift (δ) for each pure alkoxide is very different. This influence on δ values was assigned to the inductive +I effects. The influence of the inductive effect +I on δ values is more than the other parameters.

As general rule, with increasing the net positive charge on the silicon, an upfield chemical shift of ²⁹Si

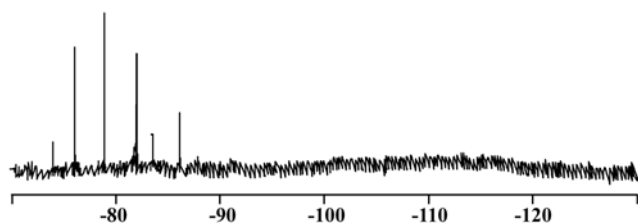


Figure 7. ²⁹Si NMR spectrum of inorganic phase (TEOS + HCl + H₂O + ETOH).

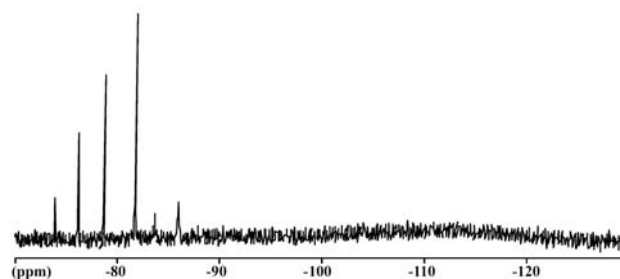


Figure 8. ²⁹Si NMR spectrum of organic-inorganic hybrid before curing.

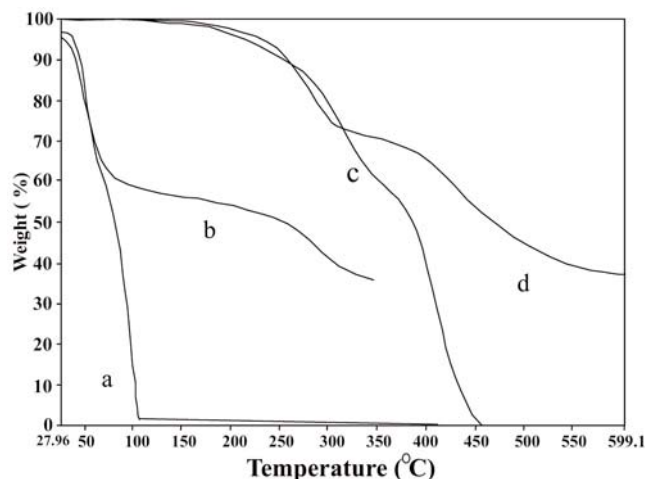


Figure 9. a) inorganic phase, b) inorganic-organic phase before curing, c) organic phase and d) inorganic-organic phase after curing.

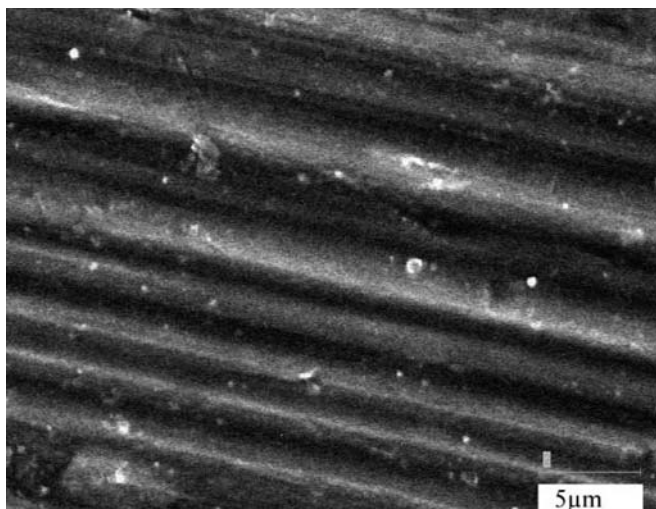


Figure 10. The SEM of Aluminum substrate

NMR is observed. More explicitly, δ values are shifted to more negative values when the positive charge on the silicon increases. From NMR results, as it can be observed in the case of TEOS, the ethoxy groups were classified like moderate electron acceptor [17].

Thermograms (TGA) of hybrid nanocomposite before and after curing and its organic and inorganic phases

In Figure 9 a TGA of the inorganic phase which was performed at heating rate of 10°C/min under nitrogen atmosphere is shown. It started to decompose at 43.5°C and lost 44.8% of its weight.

TGA of inorganic-organic hybrid phases before curing was performed at heating rate of 10°C/min under

air (Figure 9b). It started to decompose at 37.3°C and lost 49.8% of its weight. The T_d increased when the inorganic phase mixed with organic phase.

TGA of inorganic phase was performed at heating rate of 10°C/min (Figure 9c). It indicated that the sample started to decompose at 249.9°C, and lost 40.7% of its weight.

TGA of organic and inorganic hybrid after curing (Figure 9d) indicates that the hybrid nanocomposite started to decompose at 339.5°C, and lost 62.8% of its weight. Thus the cross-linking between the epoxy and silica increases thermal stability.

Morphology study of inorganic and organic hybrid system (nanocomposite) after curing

The compatibility between organic polymer and silica has a great effect on thermal, mechanical, and optical properties of hybrid matrix. For investigating the distribution of silica in hybrid matrix, the morphology of the fractured surface was studied by SEM, and was compared with aluminum surface. (cf. Figure 10,11). The large compact silica aggregates, in 100-300 nm diameter, are formed during the one stage polymerization. The two stage process with the acid prehydrolysis of TEOS leads to an acceleration of gelation and formation of more open and smaller silica structure, in 50-100 nm diameter. The average diameter is 167 nm, which indicates that the hybrid system is transparent (Figure 12).

CONCLUSION

Interpenetrating network (IPN) of organic-inorganic

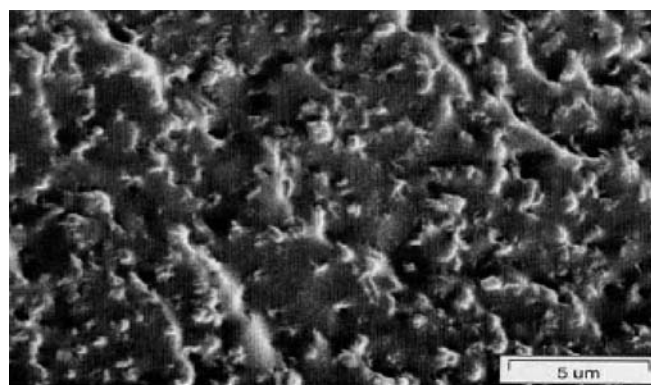


Figure 11. The SEM of fracture surfaces of inorganic-organic hybrid

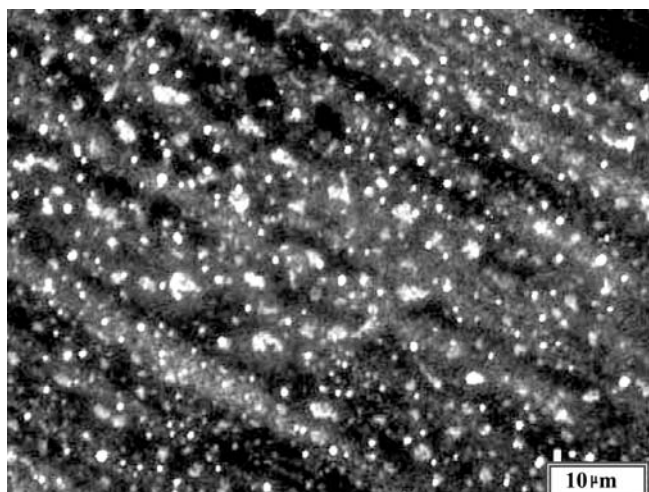


Figure 12. The SEM of hybrid inorganic-organic coating on the aluminum substrate after curing.

hybrid system composed of an organic phase that consisted of GY250 (diglycidyl ether of bisphenol A) and HY850 (aromatic amine); and an inorganic silica structure formed by sol-gel process. The organic-inorganic hybrid material (nanocomposite) was coated on the aluminum alloy (AA) substrate by dip coating method. This hybrid network possess excellent optical transparency. The obtained IPN was characterized by ^{29}Si NMR, FTIR, SEM, and TGA techniques. The ^{29}Si NMR spectrometry elucidates the type of formed molecular species and their structure. The modification of the structures of all molecular species and the bonds formed or destroyed during the sol-gel process are endorsed by using the FTIR spectroscopy. The FTIR spectra show that the Si-O-C bond is formed during the reaction and epoxy ring is opened and the peak of epoxy group is disappeared. This observation is confirmed by ATR-IR spectrometry of the aluminum substrate.

TGA results show that the cross-linking between epoxy resin and silica increases the thermal stability of the sample. SEM micrographs show that the small dispersed particles of 20-70 nm diameter are gathered in large irregular aggregates of size 100-300 nm with Average particle size of 167 nm.

REFERENCES

1. Hsiue G.H., Kuo W.J., Huang Y.P., and Jeng R.J., Microstructure and morphological characteristics of PS-

- SiO₂ nanocomposite, *J. Polym.*, **41**, 2813-2825 (2000).
2. Tong X., Tong T., Zhang Q., Feng Z., and Baotong H., Polymer/silica nanoscale hybrids through sol-gel method involving emulsion polymers I. Morphology of (butyl methacrylate)/SiO₂, *J. Appl. Polym. Sci.*, **83**, 446-454 (2002).
3. Xie T., Zhou C., Feng S., and Wang X., Study of poly(methyl methacrylate-maleic anhydride)/silica Hybrid materials, *J. Appl. Polym. Sci.*, **75**, 379-383 (2000).
4. Matejka L., Dusek K., Plestil J., Kriz J., and Lendnický F., Formation and structure of the epoxy-silica Hybrids, *J. Polym.*, **41**, 171-181 (1998).
5. Matejka L., Dukh O., and Kolarik J., Reinforcement of cross-linked rubbery epoxides by In-situ formed silica, *J. Polym.*, **41**, 1449-1459 (2000).
6. Liu Y.L., Wu C.S., Chiu Y.S., and Ho W.H., Preparation, Thermal properties, and flame retardance of epoxy-silica Hybrid resins, *J. Polym. Sci.*, **41**, 2354-2367 (2003).
7. Cardiano P., Mineo P., Sergi S., Ponterio R.C., Triscari M., and Piraino P., Epoxy-silica polymers as restoration materials part II, *polym.*, **44**, 4435-4441 (2003).
8. Ershad langroudi A, Mai C., Vigier G., and Vassoile R., Hydrophobic hybrid inorganic-organic thin films prepared by sol-gel process for glass protection and strengthening applications, *J. Appl. Polym. Sci.*, **65**, 2387-2393 (1997).
9. Sforca M.L., Yoshida I.V.P., and Nunes S.P., Organic-inorganic membranes prepared from polyether diamine and epoxy silane, *J. Membrane Sci.*, **207**, 197-207(1999).
10. Zhao Y., Cao Y., Yang Y., and Wu C., Rheological study of the sol-gel transition of hybrid gel, *Macromolecules*, **36**, 855-859 (2003).
11. Hajji P., David L., Gerard J.F., Pascault J.P., and Vigier G., Synthesis, structure, and morphology of polymer-silica hybrid nanocomposite based on hydroxyethyl methyl methacrylate, *J. Polym. Sci.*, **37**, 3172-3187 (1999).
12. Hofacker S., Mechtel M., Magerand M., and Kraus H., Sol-gel: a new tool for coatings chemistry, *Prog. Org. Coat.*, **45**, 159-164(2002).
13. Chen C., Khobaib M.K., and Curliss D., Epoxy layered-silicate nanocomposites, *Prog. Org. Coat.*, **47**, 376-383 (2003).
14. Chiang C.L.M., MA C.C., Wu D.L., and Kuan H.C., Preparation of, characterization, and properties of novalac-type phenolic/SiO₂ hybrid organic-inorganic nanocomposite materials by sol-gel method, *J. Polym. Sci.*, **41**, 905-913 (2003).

15. Boerio F.J., Structure and properties of silane primers for adhesive bonding of metals, *Polym. Preprint*, **24**, 204 (1983).
16. Boerio F.J., Infrared spectra of polymers and coupling agents adsorbed onto oxides aluminium, *Polymer Preprint*, **22**, 297 (1983).
17. Jitianu A., Britchi A., Deleanu C., Badescu V., and Zaharescu M., Comparative study of the sol-gel Process starting with different substituted Si-alkoxides, *J. Non-Crystalline Solids*, **319**, 263-279(2003).
18. Farhadyar N., Rahimi A., and Ershad Langroudi A., Synthesis and characterization of inorganic-organic hybrid produced from tetraethoxysilane and epoxy-aromatic amine, Macro 2004, IUPAC World Polymer Congress, Paris-France, 2004.